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Functional phosphorus-based π-conjugated systems: Structural diversity without multistep synthesis*

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Abstract: The synthesis and properties of linear π-conjugated systems incorporating phosphole rings are described. Their supramolecular organization in the solid state can be controlled either by chemical modifications or coordination to transition metals of the phosphorus atom. Furthermore, chemical transformations of the phosphole ring allow organizing these P-chromophores in 3D assemblies exhibiting σ–π conjugation or in organometallic ferrocene-like derivatives. Phosphole–pyridine-containing π-conjugated chromophores act as P,N-chelates toward transition-metal ions, giving rise to mono- and di-nuclear complexes. The specific properties of these complexes make them valuable materials for organic light-emitting diodes (OLEDs) and interesting building blocks for the tailoring of π-conjugated systems.

Keywords: organic materials; phosphorus heterocycles; conjugated systems; paracyclophanes; transition metals.

INTRODUCTION

Organic semiconductors have attracted considerable interest in the last decades due to their potential applications as materials for optoelectronic devices such as light-emitting diodes, field effect transistors, photovoltaic cells, or lasers [1]. The performances of these organic materials are mainly determined by their chemical structure and by their supramolecular organization in the solid state [1]. A great deal of attention has therefore been focused on tuning the structure of the organic π-conjugated materials in order to control their electronic nature [band gap, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, effective conjugation length, etc.] in such a way that it suits the desired function (electroluminescence, high charge mobility, etc.) [1]. One of the major strategies to achieve this goal is the grafting of bulky or functional side-chain substituents on the conjugated backbone. These lateral groups influence the optical and electronic properties of the materials via steric (planarity of the conjugated systems, supramolecular organization, etc.) and electronic (withdrawing or donating) effects. However, this approach requires multistep synthesis resulting in low overall yields.

Another powerful strategy for influencing and tailoring the physical properties of organic materials is to vary the chemical composition of the conjugated backbone chain by introducing, for example, heteroatomic building blocks [1,2]. Recently, it has been shown that the phosphole ring is a very inter-

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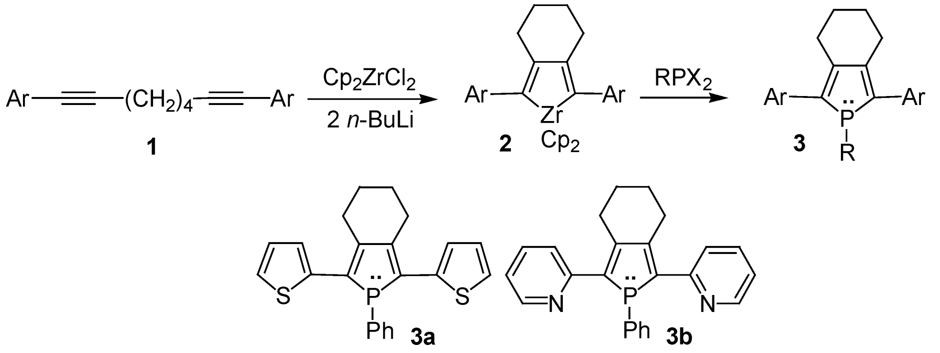
esting building block for the construction of extended π-conjugated systems [3]. In contrast to pyrrole or thiophene, the sextet of the phosphole ring is weakly delocalized and thus phospholes possess a low aromatic character and a reactive heteroatom [4]. Furthermore, due to the pyramidal shape of the P-center, the exocyclic P–R bond interacts with the endocyclic π-system leading to σ–π-hyperconjugation phenomenon [4]. The insertion of this P-heterocycle within classical π-conjugated systems results in a lowering of their HOMO–LUMO gaps [3c–e] since conjugation is enhanced for macromolecules incorporating units exhibiting low resonance energies [1]. Moreover, the phosphole building block is a potential source of further structural variations by (i) changing the nature of the P-substituent, (ii) chemical modifications of the nucleophilic P-atom, or (iii) using this P-ring as a precursor of other P-heterocycles featuring a π-system such as phosphametallocenes. Herewith, we show that chemical modifications of the phosphole ring allow us to create a structural diversity and tune the properties of P-based conjugated materials. Furthermore, we describe our recent works devoted to the organization of π-conjugated chromophores using phosphorus and coordination chemistry.

RESULTS AND DISCUSSION

π-Conjugated derivatives incorporating phosphole ring

Synthesis and physical properties

2,5-Di(heteroaryl)phospholes **3** (Scheme 1) were prepared via the “Fagan–Nugent method”, a general and efficient organometallic route to phosphole moieties [5]. The intramolecular oxidative coupling of functionalized 1,7-diynes **1** (Scheme 1), possessing a $(CH_2)_4$ spacer in order to obtain the desired 2,5-substitution pattern, with “zirconocene” provides the corresponding zirconacyclopentadienes **2** [3c–f,6]. These organometallic intermediates react with dihalogenophosphines to give the corresponding phospholes **3** in medium to good yields. 1-Phenylphospholes **3a,b** (Scheme 1) can be isolated as air-stable solids following flash column chromatography on basic alumina [3e].



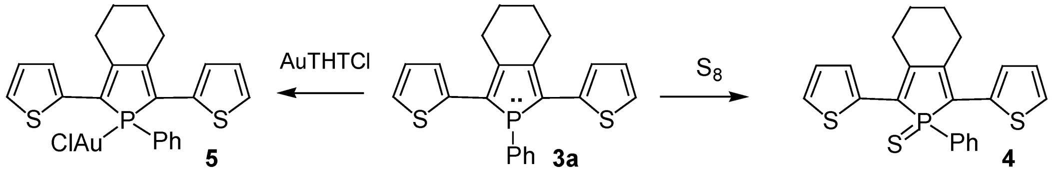
Scheme 1

σ^3,λ^3-Phospholes **3a** [3d] and **3b** [3c] (Scheme 1) bearing electron-rich and -deficient substituents, respectively, were characterized by X-ray diffraction studies. In spite of the different electronic nature of the two 2,5-substituents, compounds **3a,b** share some important structural features in the solid state. Their molecular crystal structures reveal that the three heterocycles are almost coplanar while the phosphorus atom’s environment is strongly pyramidalized [3,4]. Moreover, it is noteworthy that the carbon–carbon lengths between the rings are in the range expected for Csp^2–Csp^2 bonds. These solid-state data indicate that an efficient delocalization of the π-system takes place over the three heterocycles in oligomers **3a,b**, as supported by theoretical studies [3e,7]. The presence of an extended π-conjugated system in phospholes **3a,b** was also confirmed by the observation of a broad absorption in their

UV–vis spectrum. The energy of these absorptions, attributed to π–π* transitions [3e,7], depends dramatically on the nature of the 2,5-substituents of the phosphole ring [3e]. The values of λ_{max} and the optical end absorption λ_{onset} (the solution optical "HOMO–LUMO" gap) [3e], become red-shifted on replacing the 2-pyridyl groups (λ_{max} = 390 nm) by 2-thienyl rings (λ_{max} = 412 nm). Recent theoretical studies showed that this bathochromic shift is due to a better interaction between the HOMO of phosphole with the HOMO of thiophene, compared to that of pyridine [3e,7]. It is worth noting that the value of λ_{max} recorded for **3a** (412 nm) [3e] is considerably more red-shifted than that of the related *tert*-thiophene (355 nm) [1]. This observation is in agreement with theoretical studies predicting that heterocyclopentadienes with a low aromatic character are optimal building blocks for the synthesis of extended π-conjugated systems with low HOMO–LUMO gap [1].

Phospholes **3a,b** are also fluorophores, and their λ_{em} depend on the nature of the 2,5-substituents. A blue emission is observed for di(2-pyridyl)phosphole **3b** (λ_{em} = 463 nm), whereas the emission of di(2-thienyl)phosphole **3a** is red-shifted ($\Delta\lambda_{em}$ = 35 nm). Cyclic voltammetry (CV) revealed that the redox processes observed for all the σ^3-phospholes **3** are irreversible and that their redox properties are related to the electronic properties of the phosphole substituents [3e]. For example, derivative **3a** featuring electron-rich thienyl substituents is more easily oxidized than compound **3b**, which possesses electron-deficient pyridyl substituents.

One of the appealing properties of phosphole rings is the versatile reactivity of the endocyclic heteroatom that allows creating structural diversity in these types of systems. This feature offers a direct access to a broad range of new π-conjugated systems from single P-containing chromophores, without the need for additional multistep syntheses, as illustrated with dithienyl-phospholes **3a** (Scheme 2). The chemical modifications of the nucleophilic P-center have a profound impact on the optical and electrochemical properties of the phosphole oligomers as a whole. For example, upon modification of the σ^3-phosphole **3a** toward the neutral σ^4-derivatives **4** and **5** (Scheme 2), a red shift in their emission spectra, together with an increase and decrease of their oxidation and reduction potentials, respectively, is observed. It is also noteworthy that the quantum yields of the gold complex **5** (Φ = 14 %) is much higher than those of the corresponding phosphole **3a** (Φ = 5 %) or its thioxo-derivative **4** (Φ = 4.6 %), illustrating that the nature of the P-modification has a considerable impact on the optical properties of these fluorophores [3d,e,9].



Scheme 2

The fact that chemical modifications of the phosphorus atoms allows for a fine-tuning of the optical and electrochemical properties of phosphole-based π-conjugated systems is very promising for organic light-emitting diode (OLED) development since it would allow (i) the emission color of the devices to be varied, and (ii) a good match between the LUMO and HOMO levels and the work functions of the electrodes to be reached. Another appealing consequence of the P-modification is that the quantum yield for σ^4-thioxophosphole **4** (Scheme 2) is higher in the solid state than in dilute solution [9b]. This rather unusual behavior is probably due to the steric protection provided by the substituents (Ph, S) of the tetrahedral P-atom, which preclude a close cofacial organization of this P-chromophore in the solid state. This hypothesis is also supported by the fact that the UV–vis and fluorescence spectra of σ^4-thioxophosphole **4** in solution and in thin films are very similar; no red-shifted emission revealing excimer or aggregate formation is observed. In marked contrast, the solution and thin-film emission spectra of the gold complex **5** (Scheme 2) are different. Two broad emission bands are observed for the thin films, one at a wavelength similar to that of the solution spectrum, and a second, which is considerably red-shifted. These low-energy luminescence bands observed in the thin films most likely arise from the formation of aggregates. These results revealed that the nature of the P-moiety affects the bulk molecular environment and hence the photophysical behavior of these chromophores in the solid state; thioxophosphole derivatives are isolated luminophores, whereas gold(I) phosphole complexes form aggregates leading to broad emission spectra from both monomer and aggregate states [9]. This dichotomy shows that the presence of reactive phosphorus atoms allows for a unique molecular design to efficiently vary and control the electronic structures of π-conjugated materials. Exploitation of this method of tailoring π-conjugated systems, which is simply not possible with pyrrole and thiophene units, has led to the optimization of the properties of thiophene–phosphole co-oligomers for use as materials suitable for OLED fabrication [9].

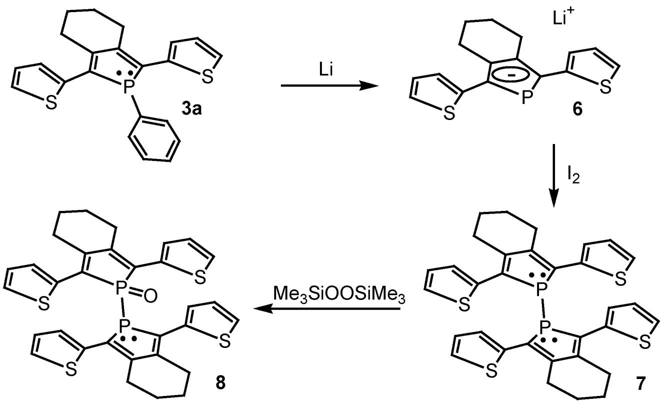
In conclusion, co-oligomers with a phosphole core exhibit very interesting properties. They are air-stable, providing that the P-substituent is a phenyl group; they exhibit low optical gap; and their electronic properties can be fine-tuned by varying the nature of the 2,5-substituents (2-thienyl or 2-pyridyl) or chemical modification of the phosphole ring.

Control of the supramolecular organization of P-based π-conjugated systems

Thienyl-capped 1,1'-diphospholes: Synthesis and hyperconjugation property

The linear derivative **3a** (Scheme 1) described above possesses extended delocalization pathway involving the dienic moiety of the phosphole ring and the thienyl units. The fact that the exocyclic P–R bond of the phosphole ring interacts with the endocyclic π-system prompted us to investigate the possible interaction of two of these π-systems through a P–P bridge. This σ–π conjugation ("through bond interaction") [10] should be favored by the fact that the P–P bond possesses a low σ–σ* gap.

Compound **7** (Scheme 3) [11], assembling two di(2-thienyl)phosphole chromophores via a P–P bond, was prepared according to the classical route to 1,1'-biphospholes [12]. This synthetic pathway implies a coupling of the corresponding phospholyl anion **6** upon oxidation with iodine (Scheme 3). An X-ray diffraction study performed on **7** revealed a P–P single bond [2.224(1) Å] and showed that the P-atoms are strongly pyramidalized [Σ bond angles, 293.7°] [11]. It is noteworthy that the bond lengths and valence angles of the organophosphorus frame of **7** compare with those of the 2,5-dithienylphosphole **3a** [3e,11].



Scheme 3

Theoretical studies have shown that the interaction of two π-systems through a σ-bridge (hyperconjugation) results in a splitting of the HOMO and LUMO of these π-systems. This induces a narrowing of the HOMO–LUMO gap and an increased density of states [10], two features which can be observed by UV–vis spectroscopy. Hence, it is of interest to compare the UV–vis spectrum of **3a**, having only one π-system, and **7** having two π-systems connected by the P–P bridge. The absorption spectrum of **3a** shows only one absorption due to a π–π* transition (412 nm) (Fig. 1). In contrast, several bands have been recorded for **7** with one red-shifted broad shoulder (λ_{onset} = 560 nm) (Fig. 1) [11]. These UV–vis data revealed an interaction of the two π-systems through the σ-(P–P) bridge in **7**. This conclusion has been confirmed by theoretical studies showing a splitting in energy of the LUMO and HOMO levels [11]. Furthermore, the LUMO of **7** is the anti-bonding combination and the LUMO+1 is the bonding combination, a behavior which is characteristic for through-bond coupling of two π-systems over an odd number of σ-bond [10a].

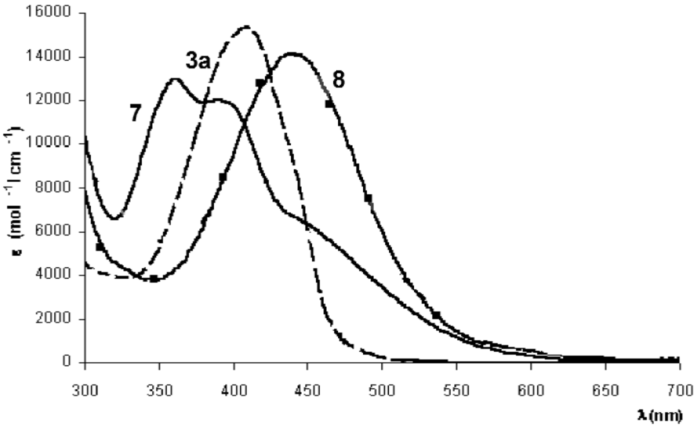


Fig. 1 Absorption spectra of **3a** (– – –), **7** (—), **8** (-■-) in CH_2Cl_2.

The chemical modifications performed of the σ^3,λ^3-P-atoms of thienyl-capped chromophore **7** (Scheme 3) offer a way to diversify their properties. For example, the band onset of the UV–vis spectrum of derivative **8** (Scheme 3), which is readily obtained using a stoichiometric amount of bis(trimethylsilyl)peroxyde, is bathochromic-shifted compared to that of 1,1'-biphosphole **7** (Fig. 1) [11]. This narrowing of the optical HOMO–LUMO gap strongly suggests that the modified σ-P–P bridge still interacts with the two π-systems by the hyperconjugative effect.

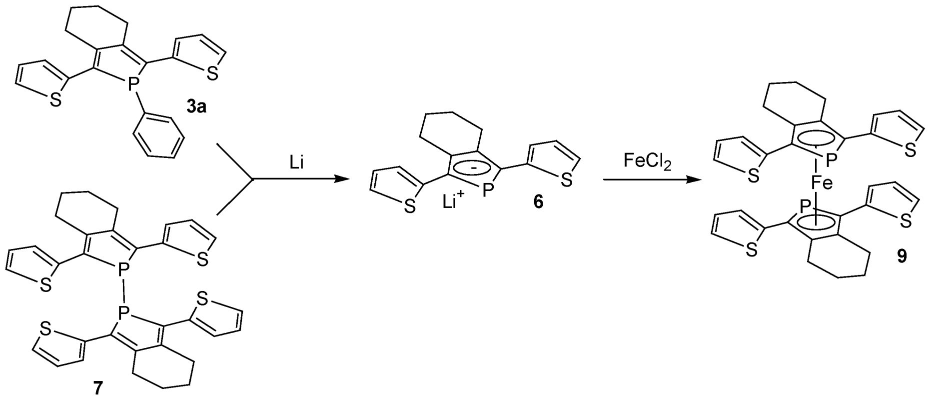
In conclusion, the P–P bond is an efficient σ-bridge to provide an electronic interaction between π-conjugated chromophores. The presence of σ^3,λ^3-P-atoms gives the opportunity to perform chemical modification influencing the physical properties of these assemblies.

Organization of P-based π-systems within a ferrocene-like structure

The phosphole ring can also be a precursor of phosphametallocenes featuring two π-systems organized around a metal center. The phosphametallocenes are of particular interest since they possess properties which are completely different from those of phospholes. Firstly, they feature a fully delocalized (aromatic) endocyclic π-system and a sp^2-hybridized P-atom exhibiting some electrophilic character [13]. Secondly, the LUMO of phosphametallocenes has an appreciable ligand character, whereas the HOMO exhibits an essentially pure metal character [13e].

The target 1,1'-diphosphaferrocene **9** has been prepared via a classic two-step sequence (Scheme 4) [4a,b,13]. The highly moisture-sensitive phospholyl anion **6** is obtained either by reductive cleavage of the P–Ph bond of the corresponding 1-phenylphosphole **3a** or of the P–P bond of

1,1-diphosphole **7** (Scheme 4) [14]. The route using **7** is more convenient since it avoids the formation of phenyl-containing by-products. The phospholyl anion **6** is then converted into the compound **9** upon reaction with $FeCl_2$ (Scheme 4) [14]. The 1,1-di-phosphaferrocene **9** can be isolated as an air-stable derivative in a satisfactory yield following purification (ca. 67 %) by crystallization. Note that the main by-product formed along the diphosphaferrocene is the 1,1-diphosphole **7.**



Scheme 4

An X-ray diffraction study performed on **9** revealed a C_{2h} conformation with the two P-atoms pointing in opposite direction. The two di(2-thienyl)phospholyl moieties are almost planar (twist angles: 0.5°–12.9°), indicating that the compound **9** possesses planar π-conjugated systems as observed for the corresponding 2,5-dithienylphosphole **3a** (twist angles: 12.5° and 16.2°). The UV–vis spectrum presents an intense band between 350–450 nm along with a red-shifted broad shoulder (Fig. 2). The band of high energy is mainly ligand-centered, whereas those of lower energy can be assigned to ligand–metal charge transfer. It is noteworthy that the λ_{max} of phosphaferrocene-based π-conjugated systems are blue-shifted compared to the corresponding phosphole-based derivatives **3a** (Fig. 2). This increase of the "optical" HOMO–LUMO gap of the π-system can be attributed to the fact that phospholyl ligands exhibit a higher aromatic character than phospholes. No fluorescence behavior was observed for the 1,1'-diphosphaferrocene compound **9** in degassed THF or CH_2Cl_2 solutions.

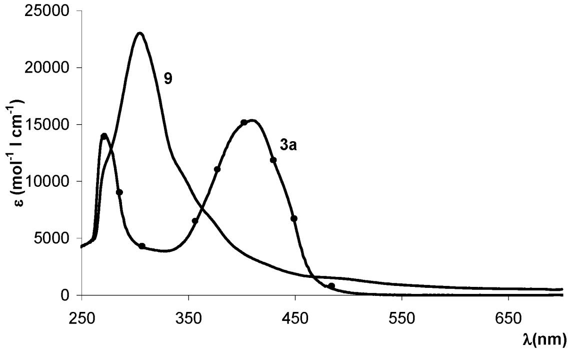


Fig. 2 Absorption spectra of **3a** (-●-), **9** (-) in CH_2Cl_2.

The electrochemical behavior of derivative **9** was investigated by CV. This compound undergoes a first reversible oxidation (+0.13 V) which is assigned to a $Fe^{2+} \rightarrow Fe^{3+}$ process [15] followed by a second and irreversible oxidation process occurring at 1.18 V. This second oxidation process probably involves the terminal thiophene rings which are known to undergo irreversible oxidation in this potential range [1]. The first oxidation of the di(2-thienyl)phospholyl moiety of **9** occurs at more anodic potential compared to di(2-thienyl)phosphole **3a** ($E^\circ = +0.40$ V vs. Fc/Fc^+) [3e], probably due to the preliminary oxidation of the Fe-center. It is noteworthy that no anodic electropolymerization process was observed with compound **9** [14].

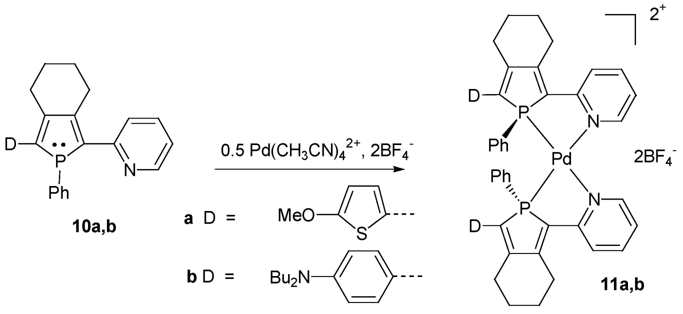
In conclusion, the properties of the 1,1'-diphosphaferrocene **9** differ markedly from those of the phosphole derivative **3a** due to the profoundly different electronic nature of these two P-building blocks. These results illustrate the potential of P-building blocks to create structural diversity and to tune the physical properties of π-conjugated systems.

Spatial organization of π-conjugated systems using coordination chemistry

Compared to organic molecules, metal complexes offer a larger variety of molecular structures and a diversity of electronic properties due to variation of metal coordination sphere or oxidation number [16]. Since it is well known that phospholes behave as classical two-electron donor tertiary phosphanes toward transition metals [4], we have investigated ahead the coordination chemistry of 2-(2-pyridyl)phospholes with the aim to use the heteroditopic nature of these ligands to organize π-systems in the coordination sphere of transition metals and also to prepare polymetallic species.

Control of the arrangement of heteroditopic phosphole-based dipoles upon coordination

The ligand behavior of phospholes can be used for the synthesis of multipolar NLOphores. Phospholes **10a** and **10b** (Scheme 5), bearing an electron-deficient pyridine group and a classic electron-donor group at the 2- and 5-positions, respectively, have been prepared according to the Fagan–Nugent method [5,17]. They exhibit moderate NLO activities ($\beta_{1.9\mu m}$, ca. 30.10^{-30} e.s.u.) compared to classical chromophores such as Dispersed Red 1 (DR1) (β, 50.10^{-30} e.s.u.) [17]. These low values are consistent with the weak acceptor character of the pyridine group. The attractiveness of dipoles **10a** and **10b** in NLO lies into their P,N-chelate behavior toward d^8 metal centers such as Pd(II) [18,19]. 2-(2-Pyridyl)phospholes **10a,b** reacted with $[Pd(CH_3CN)_4][BF_4]_2$ giving rise to the corresponding complexes **11a,b** (Scheme 5). In accordance with the *trans*-influence [20], heteroditopic P,N-dipoles **11a,b** undergo a stereoselective coordination imposing a close parallel alignment of the dipoles on the square-planar d^8 palladium template. Thus, the *trans*-effect can overcome the natural *anti*-parallel alignment tendency of dipolar chromophores at the molecular level. Complexes **11a,b** exhibit fairly high NLO activities with $\beta_{1.9\mu m}$ values reaching $170–180 \times 10^{-30}$ e.s.u. These values are much higher than the sum of the contributions of two sub-chromophores **10a,b**. The enhancement of the NLO activity upon coordination was tentatively attributed to ligand-to-metal-to-ligand charge transfers that contribute coherently to the second harmonic generation [17]. In conclusion, coordination chemistry offers a simple synthetic methodology for controlling the in-plane parallel arrangement of P,N-dipoles in a molecular assembly.

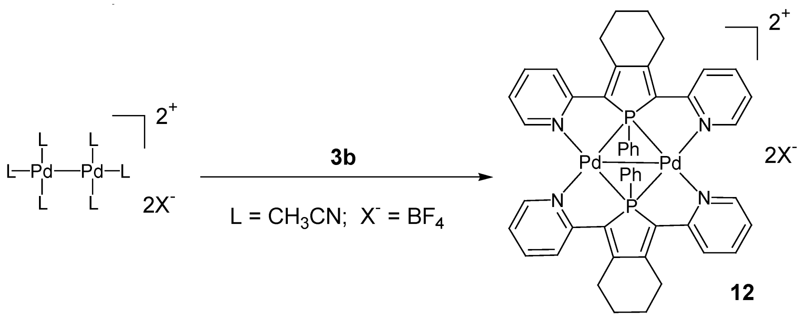


Scheme 5

Supramolecular organization of π-conjugated chromophores via coordination chemistry: Synthesis of [2.2]-paracyclophane analogs

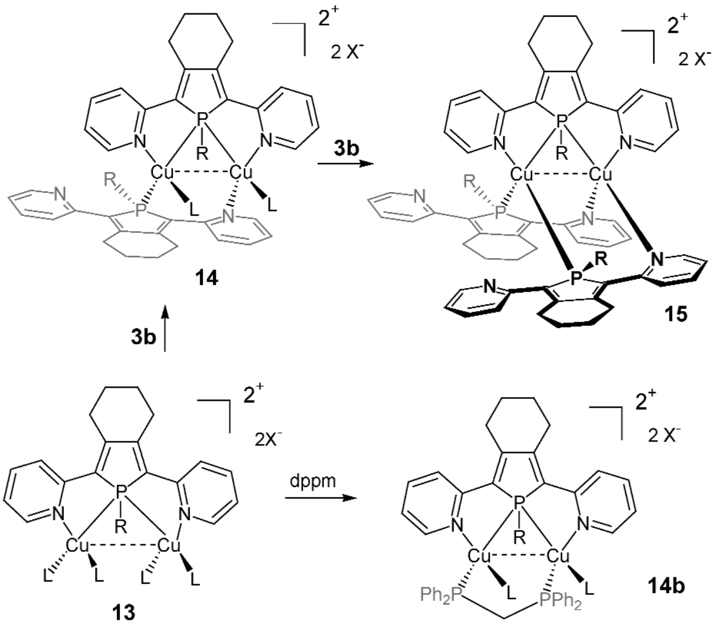
The synthesis of π-stacked molecular assemblies is of great importance in understanding the electronic interactions between individual chromophores. One fruitful approach to probe cofacial π–π interactions involves the assembly of chromophore pairs into [2,2]paracyclophanes. These molecules provide incisive insights into bulk properties of conjugated systems and are suitable π-dimer models. However, straightforward routes to these assemblies as well as for tailoring their structure remain a challenge to chemical synthesis. Hence, we have investigated a novel synthetic route to [2,2]paracyclophanes using supramolecular coordination-driven chemistry. Following the concepts of the "directional-bonding approach" [21], the construction of metalloparacyclophanes with π-stacked walls requires a bimetallic clip possessing two cis coordinatively labile sites that are closely aligned. We have prepared this type of molecular clip using the unique coordination behavior of 2,5-bis(2-pyridyl)phosphole **3b**.

The reaction of **3b** with $[Pd_2(CH_3CN)_6][BF_4]_2$ afforded complex **12** (Scheme 6) [19]. In this derivative, the Pd(I) dication contains two square-planar metal centres capped by two 2,5-bis(2-pyridyl)phospholes **3b** acting as 6-electron μ-1kN:1,2kP:2kN donors as demonstrated by the X-ray diffraction study. The P-moiety of **3b** bridges the two Pd(I) via a symmetrically bridging phosphane coordination mode [Δ(Pd–P) = 0.01 Å]. This coordination mode is very rare and was observed previously only in the case of a family of Rh(I) complexes [22]. Theoretical calculations have allowed identifying that Pd–Pd and Pd–P bonds in **12** are highly delocalized. This unusual bridging coordination mode has been exploited for the synthesis of the target molecular clips required for the synthesis of [2,2]paracyclophane analogs using supramolecular coordination-driven chemistry.



Scheme 6

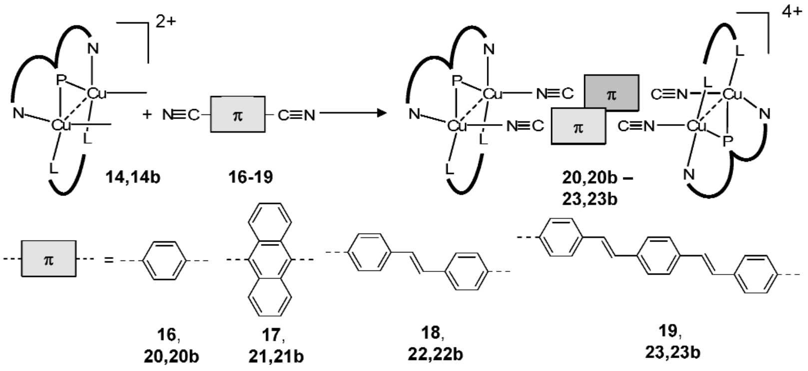
The target bimetallic clips possessing two cis coordinatively labile sites that are closely aligned was obtained by assembling Cu(I) centers with 2,5-bis(2-pyridyl)phosphole **3b**. Firstly, complex **13** (Scheme 7) was obtained by reacting two equivalents of Cu(I) ion with one equivalent of **3b** [23]. In this compound, the P-atom of 2,5-bis(2-pyridyl)phosphole **3b** binds the two Cu(I) atoms via a bridging coordination mode. Addition of one and two equivalents of **3b** to complex **13** afforded the novel derivatives **14** and **15**, respectively (Scheme 7). The incoming ligands **3b** act as P,N chelates involving the phosphorus atom of the phosphole ring and the nitrogen atom of one of the two pyridine groups. Hence, the acetonitrile ligands of complexes **13** and **14** can be easily displaced by donors without decoordination of the bridging P-ligand. This result opens the route to the synthesis of metallo[2.2]paracyclophanes by self-assembly processes using the molecular clip **14** and its dppm analog **14b** [24] (Scheme 7). These two complexes possess two acetonitrile ligands that have a *cisoid* arrangement. Furthermore, the bridging coordination mode of the phosphole ligand **3b** imposes a short intermetallic distance [**14**, 2.555(1) Å; **14b**, 2.667(1) Å] resulting in a close proximity of the two kinetically labile acetonitrile ligands (N–N distances, ca. 3.2 Å).



R = Ph, L = CH_3CN, X = PF_6^-

Scheme 7

Bimetallic derivatives **14,14b** reacted with linear homoditopic ligands **16–19** incorporating π-conjugated systems affording the derivatives **20–23b** (Scheme 8). X-ray diffraction studies of these supramolecular assemblies showed that the metric data of the dimetallic clips **14,14b** do not change significantly upon their incorporation into the self-assembled structures, demonstrating the conformation rigidity of the Cu(I)-based subunits. In all cases, the four Cu atoms lie in the same plane defining a rectangle and the aromatic moieties of the chromophores are parallel as result of hindered rotation. Moreover, due to the short Cu(I)–Cu(I) intermetallic distance imposed by the bridging phosphine coordination mode, the aromatic moieties of the ditopic ligands **16–19** participate in face-to-face π-interactions (phenyl centroid–centroid distances: 3.4–3.5 Å) with small lateral offsets. The dimensions of these rectangles are fixed by the size of the ditopic ligands and reach 18.1 Å for **22,22b** and 25.2 Å for **23** (Cu–Cu distances) with an overall dimension of **23** of about 39.0 Å in length [24].



Scheme 8

These results show that, in spite of the repulsive interactions between the π-clouds of the homoditopic ligands, the molecular clips **14,14b** can force face-to-face π-stacking of aromatic derivatives upon coordination into well-defined supramolecular metalloparacyclophanes. Hence, due to their rigidity and unique topology, complexes **14,14b** are unique building blocks for the synthesis of π-stacked molecular assemblies having a [2.2]paracyclophane-like topology. This result opens appealing perspective for the design of multifunctional molecular material via this supramolecular assembling approach. Moreover, the stacking pattern of the metalloparacyclophanes **22,22b**, and **23** is remarkable. These supramolecular rectangles make columns with short intermolecular distances (ca. 3.6 Å). In these columns, the cationic parts of the rectangles have a parallel-displaced arrangement along the *a*-axes. Unique infinite columnar stack resulting from *intra*- and *inter*-molecular π–π interactions of (*para*-phenylenevinylene)-based chromophores **18** and **19** are thus observed at the macroscopic scale with these novel metalloparacyclophanes (Fig. 3) [24].

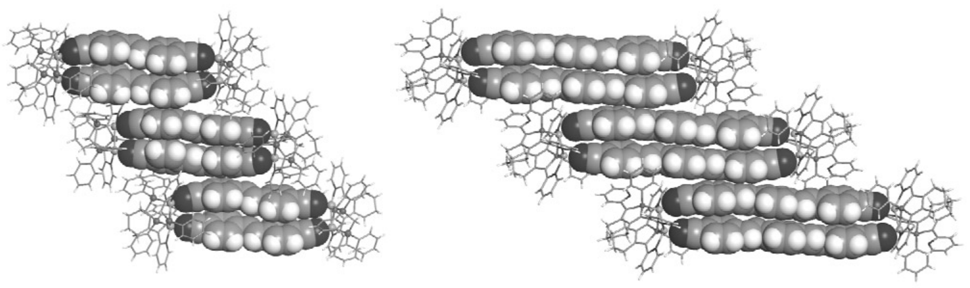


Fig. 3 Views of the packing of **22b** and **23** along the *a*-axes (H atoms, counteranions, and solvent molecules have been omitted for clarity).

In conclusion, complexes **14,14b** are versatile molecular clips for organizing π-conjugated systems in supramolecular assemblies having a [2.2]paracyclophane-topology. The rational and straightforward synthetic approach to a variety of nanoscale π-stacked metalloparacyclophanes based on molecular self-assembly can be applied to virtually any cyano-capped chromophores. Moreover, organization of the π-conjugated chromophores is observed at two hierarchical levels, the first within the metalloparacyclophanes and the second in infinite one-dimensional stacks of these metalloparacyclophanes.

CONCLUSION

Phosphole-based π-conjugated systems are attractive because of the flexibility available for fine-tuning their electronic properties and supramolecular organization through the manipulation of their structures. This is nicely illustrated by the fact that chemical modification of the P moiety affects the bulk molecular environment and hence the photophysical behavior of these chromophores in the solid state. Furthermore, the possibility to coordinate the phosphole moiety to transition metals considerably extends the potential of these P-based conjugated systems. For example, efficient NLO-phores and supramolecular metallo[2.2]paracyclophanes have been obtained by exploiting the coordination behavior of phosphole-pyridine bi- and tri-dentate ligands. The results presented in this paper demonstrate the versatility provided by the exploitation of P chemistry in the field of π-conjugated systems and are the basis for further development of P materials for optoelectronic applications

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